

*Environmental Research in China*RESISTANT DESORPTION OF HYDROPHOBIC ORGANIC CONTAMINANTS IN  
TYPICAL CHINESE SOILS: IMPLICATIONS FOR LONG-TERM FATE AND  
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**Abstract**—Soil contamination is an enormous problem in China and severely threatens environmental quality and food safety. Establishing realistic soil quality standards is important to the management and remediation of contaminated sites and must be based on thorough understanding of contaminant desorption from soil. In the present study, we evaluated sorption and desorption behaviors of naphthalene, phenanthrene, atrazine, and lindane (four common soil contaminants in China) in two of the most common Chinese soils. The desorption of these compounds exhibited clear biphasic pattern—a fraction of contaminants in soil was much less available to desorption and persisted much longer than what was predicted with the conventional desorption models. The unique thermodynamic characteristics associated with the resistant-desorption fraction likely have important implications for the mechanism(s) controlling resistant desorption. Experimental observations in the present study are consistent with our previous work with chlorinated compounds and different adsorbents and could be well modeled with a biphasic desorption isotherm. We therefore suggest that more accurate biphasic desorption models should be used to replace the conventional linear sorption/desorption model that is still widely adopted worldwide in contaminant fate prediction and soil quality standard calculations.

**Keywords**—Resistant desorption   Persistence   Availability   Soil quality standards   Soil contamination

## INTRODUCTION

Soil contamination is an enormous problem in China and severely threatens environmental quality and food safety. The State Environmental Protection Administration of China reported that, based on incomplete investigation, 150 million hectares (nearly one-tenth) of the nation's arable land was contaminated, and over 30 million hectares of agricultural land was irrigated using wastewater ([http://www.sepa.gov.cn/xcyj/zwhb/200607/t20060718\\_78512.htm](http://www.sepa.gov.cn/xcyj/zwhb/200607/t20060718_78512.htm)). Polycyclic aromatic hydrocarbons (PAHs), pesticides, and metals are the most common soil contaminants in China. For example, China was one of the largest producers and users of lindane in the 1980s and produced approximately 5,000 tons of atrazine each year [1,2]. Results from a recent investigation in Tianjin show that concentrations of total hexachlorocyclohexane (HCH) isomers in 188 surface soil samples ranged from 1.3 to 1,095  $\mu\text{g/kg}$ , with a median concentration of 45.8  $\mu\text{g/kg}$  [3]. Tao et al. [4] reported that total concentrations of 16 PAHs in agricultural soil in the Tianjin area ranged from 1.08 to 6.26  $\text{mg/kg}$ . One of the major ongoing efforts in improving the nation's soil quality and safety is the development of realistic soil quality standards for common organic pollutants in soil because currently only standards for metals, HCHs, and DDT are available.

Desorption of contaminants from soil is a critical process controlling the availability of soil contaminants and thus the risk associated with contaminated soil. Although numerous

studies have been conducted to understand the interaction between common organic contaminants and soil/sediment, some of the fundamental mechanisms remain unclear. In particular, more accurate desorption models are needed to better predict the fate, exposure, and risk of contaminated soil and to set more accurate soil quality standards. Numerous studies have shown that only a fraction of contaminants in soil can readily desorb, whereas desorption of the remaining fraction is very difficult and does not follow the conventional sorption/desorption models (a phenomenon typically referred to as resistant desorption or sequestration [5–9]). However, the conventional sorption/desorption models, which are based on the assumption that all contaminants in soils are equally available to desorption, is still widely used in fate and transport prediction and soil quality standard calculations. This oversimplified approach often causes difficulties and confusions in soil pollution management and remediation.

In our previous studies, we examined desorption of chlorinated benzenes, polychlorinated biphenyls (PCBs), and PAHs from natural soils, sediments, and surrogate adsorbents [10,11]. All of the chemical-adsorbent combinations exhibited biphasic desorption patterns in that desorption followed the conventional linear isotherm in the high-concentration range but deviated significantly in the low-concentration range [12,13]. The resistant-desorption fraction exhibited unique thermodynamic and kinetic properties that are different from those of the readily desorbable fraction, and the overall desorption could be well predicted with a biphasic desorption model that combines the conventional linear model and a quasi-Langmuir model [9]. In the present study, we further ex-

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amined the sorption and desorption of four common soil contaminants in two of the most common Chinese soils. The contaminants included two PAHs, naphthalene and phenanthrene; a widely used herbicide, atrazine; and one of the most widely used pesticides, lindane. The soils are “meadow soil” and “black soil,” two of the most common soil types in China. The experimental results were compared with the predictions of a biphasic desorption model developed in our previous work. The paper also discusses implications for the mechanism(s) controlling resistant desorption, the applicability of our biphasic desorption model as a general model to better predict desorption as well as the validity of using biphasic desorption models in fate-transport prediction and soil quality standard calculations.

## MATERIALS AND METHODS

### Materials

Two of the most common Chinese soils—“meadow soil” (soil A) and “black soil” (soil B)—were used as sorbents. Soil collected from the surface layer (20 cm) was air-dried at room temperature, crushed, and sieved through a 1-mm sieve. Soil A is slightly acidic (pH 6.0) and contains 27% clay, 37% silt, and 36% sand. Soil B is more basic (pH 7.8) and contains 35% clay, 44% silt, and 21% sand. The fractional organic carbon ( $f_{oc}$ ) values of soil A and soil B are 0.010 and 0.021, respectively. The two soils do not contain detectable quantity of contaminants studied in the present research.

Naphthalene, phenanthrene, and atrazine were obtained from Sigma-Aldrich (St. Louis, MO, USA), and lindane was obtained from AccuStandard (New Haven, CT, USA). Aqueous solutions of adsorbates and electrolyte solutions were prepared in deionized water and contained 0.01 M  $\text{CaCl}_2$ , 0.01 M  $\text{NaCl}$ , and 0.01 M  $\text{NaN}_3$  (for PAH and lindane experiments) or 0.002 M  $\text{HgCl}_2$  (for atrazine experiments). Either  $\text{NaN}_3$  or  $\text{HgCl}_2$  was used as the inhibitor for bacterial growth. All organic solvents were either gas chromatography/mass spectrometry or high-performance liquid chromatography (HPLC) grade.

### Analytical methods

Naphthalene, phenanthrene, and atrazine were analyzed with a Waters 1100 HPLC equipped with a binary HPLC pump 1525 (Waters, Milford, MA, USA) and a symmetry reversed-phase C18 column ( $4.6 \times 150$  mm). The detector for naphthalene and phenanthrene was a Waters 2475 fluorescence detector, and that for atrazine was a Waters 2487 Dual  $\lambda$  absorbance detector. Lindane was analyzed with an Agilent 6890N gas chromatograph with electron capture detector (Agilent Technologies, Santa Clara, CA, USA) equipped with an HP-5 capillary column ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$ ).

### Sorption and desorption experiments

Sorption and desorption experiments were carried out in 40-ml amber glass vials with Teflon®-lined screw caps (Fisher Scientific, Pittsburgh, PA, USA), using procedures similar to those in our previously published papers [9–12]. The experimental protocols are summarized in Table 1, and individual experiments were coded in the following way. Each of the seven chemical–soil combinations was given an Arabic number, from 1 to 7. For each chemical–soil combination, five to eight individual sorption experiments were conducted to obtain the sorption isotherm; this set of sorption experiments is denoted with a letter A. On completion of the sorption experiments of each chemical–soil combination, one to four vials

used in the sorption experiments were taken to conduct repetitive desorption experiments. These individual desorption experiments are denoted as D1 to D4. For example, experiment 1-A means experiment 1 (naphthalene, soil A), sorption experiments, and experiment 5-D2 means experiment 5 (atrazine, soil A), desorption experiment 2.

In each sorption experiment, 3 to 5 g of soil were added to a 40-ml vial that was then filled with an aqueous solution of a contaminant to leave minimal headspace. The potential loss due to volatilization was negligible—for naphthalene, the most volatile of the chemicals studied (air–water partition constant =  $10^{-1.74}$  [14]), even if as much as 1 ml of headspace was present, the fraction in the headspace would be only 0.00045 at room temperature. The vials were tumbled at 1 to 2 rpm for 5 to 7 d; the time required to reach sorption equilibrium was predetermined. Afterward, the vials were centrifuged at 3,000 g for 30 min, and the supernatant was withdrawn to analyze equilibrium concentrations.

In most desorption experiments, desorption was initiated by successively replacing 90% of supernatant with contaminant-free electrolyte solution. Additionally, Tenax® (Alltech Associates, Deerfield, IL, USA) was used in selected steps in experiment 7-D1 to facilitate desorption. The equilibrium time for each repetitive desorption step was 3 to 5 d, which was predetermined (by letting contaminated soil equilibrate with contaminant-free electrolyte solution for more than 15 d and checking aqueous-phase concentrations at varied time intervals). At the end of each desorption step, the vials were centrifuged at 3,000 g for 30 min, and the supernatant was withdrawn to analyze contaminant concentration. Tenax-enhanced desorption was conducted with procedures developed in a previous study [10]. Approximately 0.5 g Tenax was added to the vial. Then the vial was tumbled for 3 d, and Tenax was withdrawn and extracted with acetone to determine the amount of lindane desorbed. In experiments 3-D1 and 4-D1, contaminated soil was prepared with a continuous sorption method instead of a one-step sorption (as in the other desorption experiments). Approximately 2 g of soil, approximately 40 ml of electrolyte solution, and a certain amount of solid phenanthrene sealed in a dialysis membrane bag (with a molecular-weight cutoff of 1,000) were enclosed in a U.S. Environmental Protection Agency (U.S. EPA) vial. The amount of phenanthrene inside of the dialysis bag was precalculated so that the maximum sorption capacity could be reached. The vials were tumbled at 1 to 2 rpm for 30 d. Afterward, the vials were centrifuged at 3,000 g for 30 min, and both the aqueous- and the solid-phase concentrations were analyzed. It has been demonstrated in our previous studies that Tenax-enhanced desorption and dialysis bag-assisted sorption have little effect on the sorption/desorption behaviors [10].

A method similar to that developed by Huang and Pignatello [15] was used to determine solid-phase concentrations (mainly at the end of the multiple desorption steps for mass-balance check). For naphthalene, phenanthrene, and atrazine, ~1 g wet soil was transferred to a 20-ml glass vial, and methanol–water solution (4:1 by volume) was added to leave approximately 1 ml of headspace. The vial was crimp-sealed and horizontally shaken in a water bath at 85°C for 4 to 8 h. Afterward, the vials were centrifuged at 3,000 g for 30 min, and the supernatant was withdrawn for analysis. For lindane, a hexane–acetone mixed solvent (1:1 by volume) was used, and the samples were sonicated for 2 h before shaken in the water bath. Extraction efficiencies determined in quality con-

Table 1. Summary of adsorption and desorption experiments

Experiment no. <sup>a</sup>	Adsorption			Desorption					Final log $K_{OC}^{App\ c}$
	Soil	log $K_{OC} \pm$ standard deviation	No. of data	Initial q (mg/kg) <sup>b</sup>	Initial C (mg/L) <sup>b</sup>	Initial log $K_{OC}^{App\ c}$	Desorption steps	$f^d$	
Naphthalene									
1-A	A	$2.87 \pm 0.17$	7						
1-D1	A			48.0	9.69	2.69	10	1	5.02
1-D2	A			33.7	6.10	2.74	10	1	4.94
1-D3	A			1.42	0.218	2.82	4	0.13	
1-D4	A			0.622	0.0370	3.22	2	0.10	
2-A	B	$2.84 \pm 0.07$	5						
2-D1	B			95.1	7.41	2.79	8	1	4.93
2-D2	B			2.01	0.149	2.81	5	0.10	
Phenanthrene									
3-A	A	$4.33 \pm 0.05$	8						
3-D1 <sup>e</sup>	A			76.6	0.975	3.89	11	1	5.14
3-D2	A	$4.33 \pm 0.04$	7	10.4	0.0560	4.27	9	1	
4-A	B								
4-D1 <sup>e</sup>	B			129	0.801	3.88	48	1	5.01
Atrazine									
5-A	A	$2.21 \pm 0.15$	7						
5-D1	A			9.62	9.51	2.00	13	1	5.01
5-D2	A			9.58	9.53	2.00	11	1	5.03
5-D3	A			0.153	0.0800	2.28	5	0.020	
5-D4	A			0.0260	0.0170	2.18	2	0.005	
6-A	B	$2.21 \pm 0.08$	7						
6-D1	B			27.7	8.88	2.17	11	1	5.04
6-D2	B			27.7	8.89	2.17	12	1	5.23
Lindane									
7-A	A	$3.03 \pm 0.12$	6						
7-D1	A			24.6	2.79	2.95	13	1	5.45
7-D2	A			2.04	0.189	3.03	8	0.15	

<sup>a</sup> A and D denote sorption and desorption, respectively. For example, experiment 1-A means experiment 1, sorption experiments, and experiment 1-D1 means experiment 1, desorption experiment 1.

<sup>b</sup> Initial solid- and aqueous-phase concentrations before desorption was initiated.

<sup>c</sup> Apparent organic carbon-normalized distribution coefficient, defined as  $K_{OC}^{APP} = (q/C)/f_{OC}$ .

<sup>d</sup>  $f$  is a nondimensional factor indicating the extent that the resistant-desorption compartment is filled ( $0 < f \leq 1$ ).

<sup>e</sup> Contaminated soil samples prepared by continuous sorption using a dialysis membrane bag.

trol experiments using freshly spiked soils (with contact time ranging from 2–20 d) were 95 to 102% for naphthalene, 93 to 98% for phenanthrene, 90 to 94% for atrazine, and 90 to 101% for lindane. Mass balance was checked by comparing the initial mass in the vial to the sum of the mass left in the vial after multiple desorption and the total mass removed during desorption. The mass balance for each of the sorption and multistep desorption experiments listed in Table 1 was typically above 90 to 95%.

## RESULTS AND DISCUSSION

### Sorption and desorption

Results of the sorption and desorption experiments are summarized in Table 1 and Figures 1 to 4. The  $K_{OC}$  (organic carbon-normalized partition coefficient) values from individual sorption experiments are similar, even though wide concentration ranges were covered. The sorption isotherms shown in the figures also suggest that sorption generally followed the conventional linear model. In addition, the  $K_{OC}$  values of the same contaminant observed in the two different soils are essentially identical. Therefore, the sorption results indicate that sorption of these four chemicals to the soils was driven primarily by hydrophobic partitioning into soil organic matter.

Desorption results deviate significantly from sorption data

and clearly show that desorption was biphasic—desorption was relatively easy in the higher concentration range but became increasingly difficult with each additional repetitive desorption step. The ratio of the resistant-desorption fraction to the readily desorbable fraction varied among different experiments but was in general larger for soil samples with lower initial solid-phase concentrations. This can be understood by comparing experiment 1-D1 and experiment 1-D3 (refer to Fig. 1)—in experiment 1-D1, desorption started to deviate considerably from the sorption isotherm after four or five repetitive desorption steps, whereas the second desorption data point of experiment 1-D3 already deviates significantly from the sorption isotherm.

The apparent organic carbon-normalized distribution coefficients, the initial  $K_{OC}^{APP}$  values (before desorption was initiated), and the final  $K_{OC}^{APP}$  values for selected desorption experiments (the ones that have undergone sufficient desorption to remove most of the readily desorbable fraction) are compared in Table 1. The initial  $K_{OC}^{APP}$  values can be considered as characteristic  $K_{OC}$  values for the readily desorbable fraction. Two striking characteristics can be generalized. First, the final  $K_{OC}^{APP}$  values are significantly higher than the respective initial  $K_{OC}^{APP}$  values, and, second, the final  $K_{OC}^{APP}$  values of the seven different contaminant–soil combinations are very similar

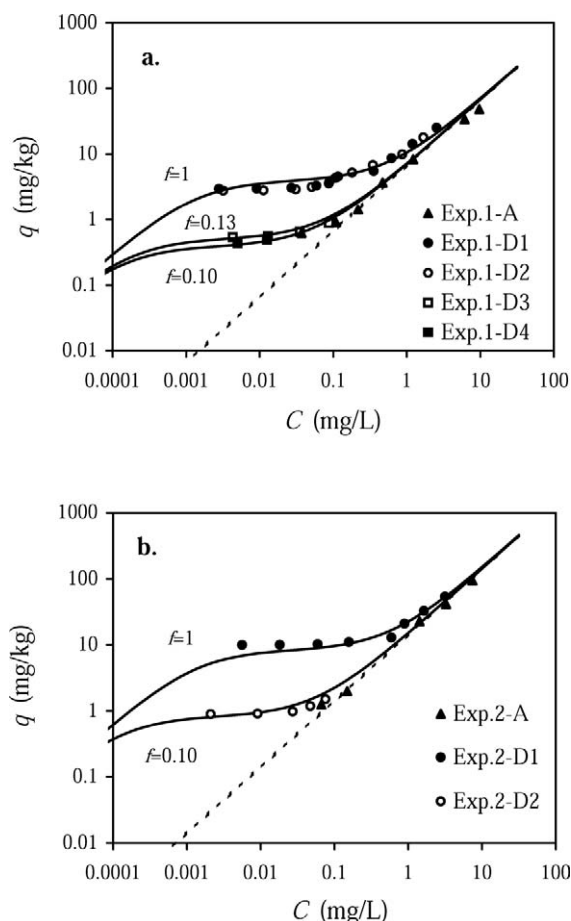


Fig. 1. Plot of model-predicted isotherms versus experimentally observed sorption and desorption results of naphthalene in soil A (a) (experiment 1) and soil B (b) (experiment 2). The solid lines are the predicted desorption isotherms using the dual-equilibrium desorption model (Eqn. 1) and parameters from Schwarzenbach et al. [14]. The dotted line is the linear isotherm plotted using the  $K_{OC}$  value obtained in sorption experiments.  $f$  is a nondimensional factor indicating the extent that the resistant-desorption compartment is filled ( $0 < f \leq 1$ ).

( $10^{5.08 \pm 0.16}$ ), although their initial  $K_{OC}^{APP}$  values differ by as much as more than two orders of magnitude. The final  $K_{OC}^{APP}$  values observed in the present study are slightly lower than those observed in our previous studies on desorption of chlorinated benzenes from a historically contaminated sediment and desorption of PAHs from soils with varied  $f_{OC}$  [9,10]. This is due to fewer desorption steps being conducted in the present study because of the difficulty in measuring accurately the sub-ppb level of concentrations. Limitations due to the experimental methods implied common limitations on the final aqueous concentration measurements, but the solid concentrations were not so constrained. Therefore, the similar final  $K_{OC}^{APP}$  values among different contaminant–soil combinations suggest a common physical phenomenon (mechanism) for the resistant desorption of different compounds, as will be discussed below and in the next section.

Similar unique characteristics associated with the desorption-resistant fraction have been observed in other studies conducted using several classes of chemicals with significantly different physical-chemical properties and various adsorbents [9,10]. The most striking characteristic was that despite the large differences in contaminant and adsorbent properties (solubility, octanol–water partition coefficient [ $K_{OW}$ ], and so on),

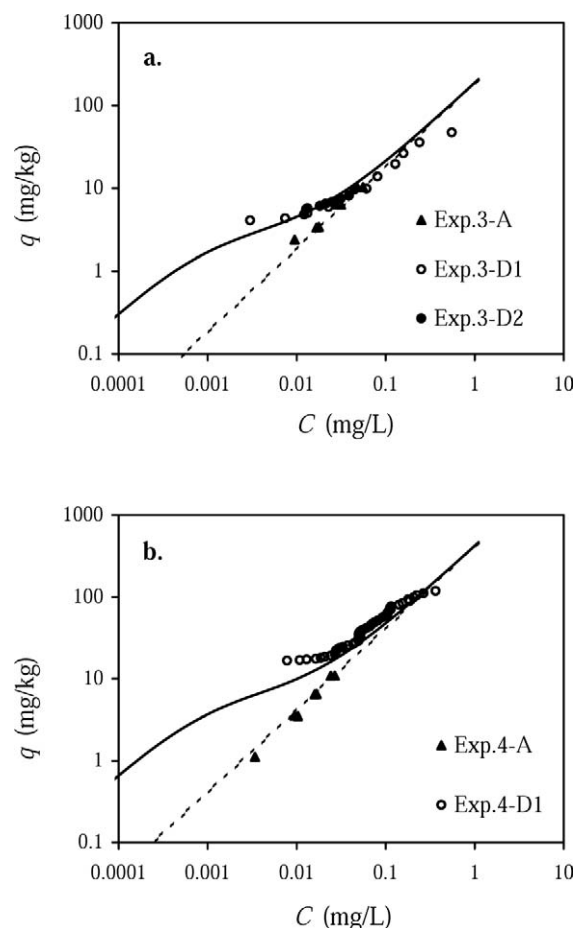


Fig. 2. Plot of model-predicted isotherm versus experimentally observed sorption and desorption results of phenanthrene in soil A (a) (experiment 3) and soil B (b) (experiment 4). The solid line is the predicted desorption isotherm using the dual-equilibrium desorption model (Eqn. 1) and parameters from Schwarzenbach et al. [14]. The dotted line is the linear isotherm plotted using the  $K_{OC}$  value obtained in sorption experiments.  $f$  is a nondimensional factor indicating the extent that the resistant-desorption compartment is filled ( $0 < f \leq 1$ ). Soil of experiments 3-D1 and 4-D1 was prepared by continuous sorption.

desorption from the desorption-resistant fraction exhibited very similar  $K_{OC}$  values and very similar desorption kinetics. Moreover, in the desorption experiments conducted with both field-contaminated sediments and laboratory-contaminated sediments with varied incubation times, we have observed negligible changes in aqueous concentration after about 7 d, even though in several desorption experiments desorption time was extended to more than six months [9,10]. These findings, along with the data obtained in the present study, indicate that sorption and desorption (of the readily desorbable and desorption-resistant fractions) are controlled by different mechanisms. While hydrophobic partitioning into the soil organic matter is the predominant mechanism for sorption, the unique characteristics of the desorption-resistant fraction indicate that the cause of resistant desorption (sequestration) cannot simply be attributed to the molecular interaction between contaminant(s) and soil components or to slow diffusion. Thus, in Figures 1 to 4, a given aqueous concentration is commonly associated with two or more different solid concentrations, one as a result of sorption only and another associated with desorption.



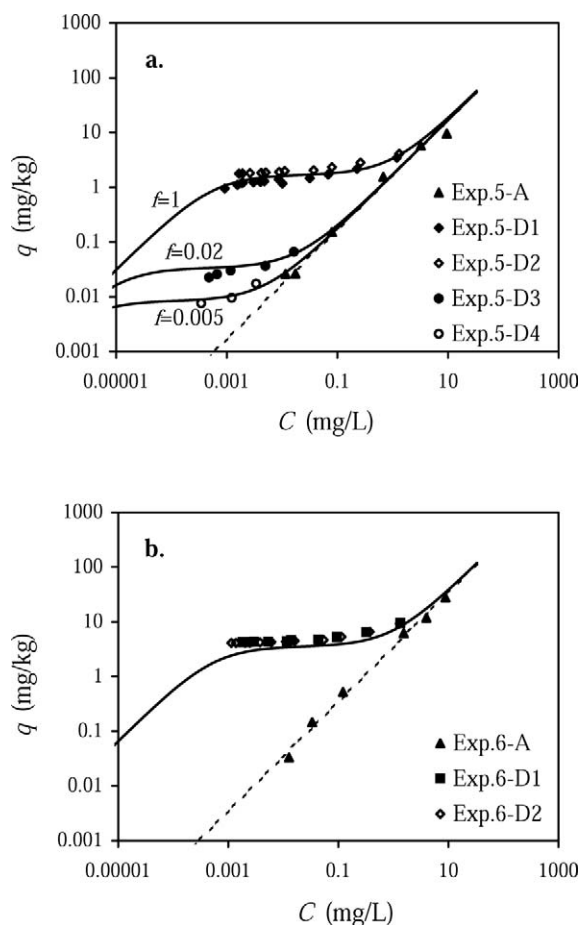


Fig. 3. Plot of model-predicted isotherms versus experimentally observed sorption and desorption results of atrazine in soil A (a) (experiments) and soil B (b) (experiment 6). The solid lines are predicted desorption isotherms using the dual-equilibrium desorption model (Eqn. 1) and parameters from Schwarzenbach et al. [14]. The dotted line is the linear isotherm plotted using the  $K_{OC}$  value obtained in sorption experiments.  $f$  is a nondimensional factor indicating the extent that the resistant-desorption compartment is filled ( $0 < f \leq 1$ ).

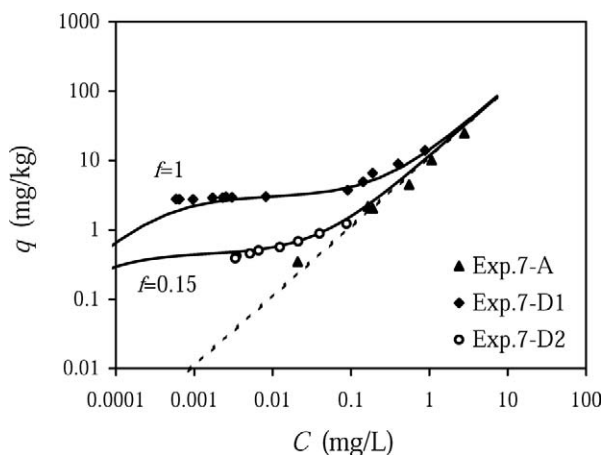


Fig. 4. Plot of model-predicted isotherms versus experimentally observed sorption and desorption results of lindane in soil A (experiment 7). The solid lines are predicted desorption isotherms using the dual-equilibrium desorption model (Eqn. 1) and parameters from Schwarzenbach et al. [14]. The dotted line is the linear isotherm plotted using the  $K_{OC}$  value obtained in adsorption experiments.  $f$  is a nondimensional factor indicating the extent that the resistant-desorption compartment is filled ( $0 < f \leq 1$ ).

A number of mechanisms have been proposed in the literature to explain this often observed resistant-desorption phenomenon. These mechanisms can be roughly categorized as mechanisms based on diffusion-limitation (e.g., slow kinetics in reaching adsorption and desorption equilibrium due to diffusion in intraparticle micropores or in organic matters) and mechanisms based on physical entrapment (e.g., the ink-bottle or sieve effect caused by postsorption conformational change of soil organic matrix, pore deformation [holes expanded or formed during sorption, causing a desorption “environment” different from the sorption “environment”], and so on) [5–9,16–21]. Accordingly, various new isotherms and kinetic models have been developed on the basis of these mechanisms [22–35]. Even though more than one mechanism might contribute to the observed resistant-desorption phenomenon, the unique characteristics associated with the desorption-resistant fraction seem to be in favor of the mechanisms based on physical entrapment within the soil organic matrix, which might better explain why desorption behaviors are independent of chemical and adsorbent properties.

#### Applicability of a biphasic desorption model

The observed desorption patterns in this study further indicate that desorption of hydrophobic organic contaminants is biphasic in nature and the extent of resistant desorption is significant; this is true even for contaminants adsorbed to soils for very short periods of time, such as those in the present study. Therefore, biphasic desorption models should be more accurate in quantifying desorption of most nonionic, hydrophobic organic contaminants after a few days of weathering.

Several research groups have developed biphasic sorption/desorption models; some of the models are kinetic based, and some are equilibrium models. Karickhoff and Morris [29] assumed that the fast and slow compartments have the same equilibrium partition coefficient and found that the characteristic time for the slow compartment is  $1/k_2$  (h) =  $0.03 \cdot K_p$  (where  $k_2$  and  $K_p$  are the kinetic constant and equilibrium partition coefficient, respectively); they also reported that for the slow compartment, the rate of sorption was similar to that for desorption. Using this criterion, the  $1/k_2$  values for the compound–soil combinations in the present study would vary from 0.05 h for atrazine with soil A to 13.5 h for phenanthrene with soil B. In two recent studies, both Sharer et al. [32] and Nkedi-Kizza et al. [33] reported  $1/k_2 = 3.8$  h for atrazine desorption from the slow compartment, with different soils. Using the radial diffusion model of Wu and Gschwend [30,31] for the soils and suspension in the present study, the half-life for sorption or for desorption is expected to be only a few seconds, but this model is known to underestimate desorption rate at early times and to overestimate rate for later times [34] and was therefore not used as a criterion for the present study. Cornelissen et al. [35] have used a two-compartment first-order empirical kinetic model to fit fast and slow desorption data. We used their model and found reasonable agreement with their fast and slow characteristic times on the order of minutes for the fast compartment and one to a few days for the slow compartment. Finally, we previously measured the desorption kinetics from the second compartment for soils similar to the ones used herein and found that after 3 to 7 d, the solution phase concentrations changed very little for at least another 180 d [10]. All these studies suggest that for the chemical–soil combinations in the present study, after a few days an equilibrium model (as discussed below) is probably sufficient

to describe the sorption and desorption data, but if the environmental interest is for shorter periods of time than a few days, it might be necessary to use one of the kinetic models.

Most of the biphasic equilibrium models are a combination of the conventional linear isotherm and a Freundlich or quasi-Langmuir isotherm [9,10,22–27]. Data obtained in the present research was compared with a Dual-Equilibrium Desorption (DED) model developed in our previous studies [10]. The DED model is based on the assumption that contaminants adsorbed in soil/sediment reside in two compartments—a readily desorbable compartment and a desorption-resistant compartment—and accordingly can be expressed as

$$q = K_{OC}^{1st} \cdot f_{OC} \cdot C + \frac{K_{OC}^{2nd} \cdot f_{OC} \cdot (f \cdot q_{max}^{2nd}) \cdot C}{(f \cdot q_{max}^{2nd}) + K_{OC}^{2nd} \cdot f_{OC} \cdot C} \quad (1)$$

where  $q$  (mg/kg) is the solid-phase concentration of the contaminant,  $C$  (mg/L) is the aqueous concentration,  $K_{OC}^{1st}$  (L/kg-OC) is the partition coefficient of the readily desorbable fraction normalized for organic carbon,  $K_{OC}^{2nd}$  (L/kg-OC) is the distribution coefficient of the resistant-desorption fraction normalized for organic carbon,  $q_{max}^{2nd}$  (mg/kg) is the maximum capacity of the desorption-resistant fraction, and  $f$  is a nondimensional factor indicating the extent that the resistant-desorption compartment is filled ( $0 < f \leq 1$ ). The value of  $K_{OC}^{1st}$  is approximately equal to the  $K_{OC}$  value observed in sorption studies (and given the high variability of  $K_{OC}$  reported in the literature, the actually measured  $K_{OC}$  should be used whenever available) but can also be estimated using common correlations (e.g., from  $K_{OW}$ , as in Schwarzenbach et al. [14]). The value of  $K_{OC}^{2nd}$  has been found to be a constant ( $\log K_{OC}^{2nd} = 5.92 \pm 0.16$ ) for all nonpolar (or apolar), nonionizable hydrophobic organic compounds, such as chlorinated benzenes and polynuclear aromatic compounds, whose interactions are dominated by London or van der Waals forces [14] and different sorbents (soils, sediments, carbonaceous materials, and so on) tested (including over 50 data sets, with varied concentrations from sub-ppb to near aqueous solubility) [9–13,36]. The  $q_{max}^{2nd}$  can be calculated with the following equation:

$$q_{max}^{2nd} = f_{OC} (K_{OW} C_{sat})^{0.534} \quad (2)$$

where  $C_{sat}$  (mg/L) is the aqueous solubility [10]. More detailed discussion on the basis and development of the DED model can be found in an earlier paper [36].

Results of the 17 desorption experiments conducted at various initial solid-phase concentrations are compared with the model predictions in Figures 1 to 4. In each figure, the DED model was plotted using the previously developed Equations 1 and 2 and parameters from Schwarzenbach et al. [14], with no attempt to fit the experimental data by modifying model parameters. The figures show that in general, the desorption results agree well with the predictions of the DED model (the solid lines in the figures), even though desorption data do not cover the very low end of the DED curves. On the contrary, the experimental observations deviate significantly from the predictions of the conventional linear model (the dotted lines in the figures), especially at relatively low concentrations. Results of experiment 4-D1 do not agree with DED model predictions as well as the other experiments. This is likely due to the accumulation of errors (especially errors from instrumental analysis) through the 47 desorption steps because the solid-phase concentrations were calculated from the measured aqueous-phase concentrations based on mass balance. None-

theless, the overall desorption pattern is still consistent with the other experiments.

Desorption experiments can be divided into two categories in terms of the initial solid-phase concentration. Figures 1 to 4 show that when desorption was initiated from a high initial solid-phase concentration (e.g., experiments 1-D1 and 1-D2 and experiment 2-D1), desorption data points fall onto the DED curve plotted using an  $f$  factor equal to one. However, when desorption was initiated from a much lower initial solid-phase concentration (e.g., experiments 1-D3 and 1-D4 and experiment 2-D2), the  $f$  factor has to be adjusted to fit the data, indicating that the resistant-desorption compartment could not be filled on a one-step sorption in these experiments. Similar conclusions can be drawn from the other desorption data sets. Contaminated soil used in experiments 3-D1 and 4-D1 was prepared in a different way—continuous sorption was used (and the maximum sorption capacity in the soil was reached), whereas a one-step sorption was used to prepare contaminated soil in the other experiments (and the maximum sorption capacity was not reached). However, the desorption results of experiments 3-D1 and 4-D1 are quite similar to the results of the desorption experiments started at high initial concentrations (e.g., experiments 1-D1 and 1-D2), especially as all the  $f$  factors are approximately equal to one. Thus, it appears that the capacity of the resistant-desorption compartment can be filled even when the overall maximum sorption capacity of the soil is not totally filled. Similar observations were reported earlier [9]. This unique property associated with the desorption-resistant compartment is likely to be the prime source of disagreement between laboratory and field observations—desorption often appears to be more resistant in the field (i.e., the so-called aging effect), and the  $f$  factor is close to one in most of these cases.

Overall, biphasic desorption models appear to have an advantage over the currently adopted sorption/desorption models. It is possible that simple biphasic desorption models, such as the DED model, might be adopted as a general model for a wide range of hydrophobic organic contaminants and natural or synthetic adsorbents. While the molecular mechanism(s) controlling resistant desorption might still remain unclear, application of biphasic models for the time being could facilitate fate/exposure prediction and risk management of contaminated sites.

#### Implications for long-term fate

The most obvious (and direct) effect of resistant desorption is that it causes contaminants to persist much longer in soil; this effect has often been observed in studies on long-term fate of common environmental contaminants and in situ remediation projects. A very common trend is that contaminant concentrations in the media of concern (e.g., surface or subsurface soil and groundwater) decrease readily after contamination occurred or during the early stage of remediation, but after the initial rapid decline, mass reduction becomes gradually slower and finally levels off to a very low constant rate, and contaminants appear to be inert to chemical reactions and microbial degradation. Accordingly, contaminants would persist in the environment for a much longer period of time than what was initially expected, causing difficulties in site management and remediation. This is the reason that persistence has been observed not only for the true persistent organic pollutants such as DDT but also for compounds commonly characterized as volatile, reactive, and less adsorptive.

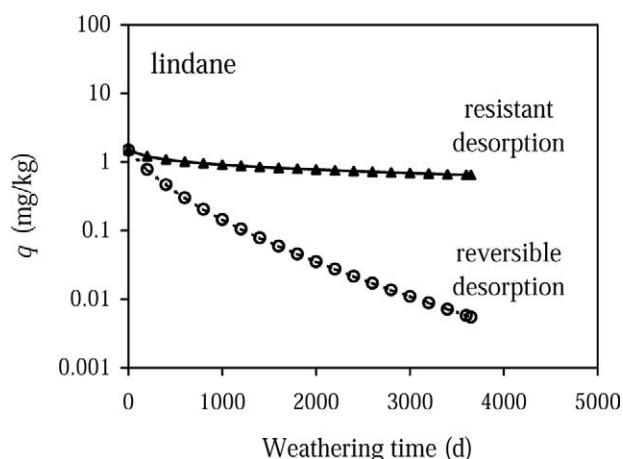


Fig. 5. Illustration of the effect of resistant desorption on long-term fate. The two curves represent changes of lindane concentration in soil with weathering time, assuming desorption follows the linear isotherm (dotted line, with the  $\circ$  symbol) and the dual-equilibrium desorption model (Eqn. 1, solid line, with the  $\blacktriangle$  symbol), respectively. The following parameters in Equation 3 were assumed:  $n = 0.3$ ,  $\rho = 1.67 \text{ g/cm}^3$ ,  $f_{oc} = 0.002$ ,  $v = 0.30 \text{ m/d}$ , and  $D = 0.035 \text{ m}^2/\text{d}$ .

The effect of resistant desorption on the long-term fate of contaminants can be quantitatively illustrated with Figure 5, which shows a simulated case of long-term fate of lindane in soil, assuming that decay is controlled by factors including uncontaminated surface infiltration (or flushing of upgradient groundwater), dispersion, and biological or chemical degradation. The two curves in the figure represent the changes of lindane concentration in soil under two different scenarios: Desorption is reversible and follows the conventional linear model, and desorption is biphasic and follows the DED model. The following equation was used to calculate the change of lindane concentration in soil with time:

$$\frac{\partial C}{\partial t} + \frac{\rho}{n} \frac{\partial q}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (3)$$

where  $D$  is the hydrodynamic dispersion coefficient ( $\text{m}^2/\text{d}$ ),  $v$  is the average surface water infiltration rate or groundwater seepage velocity ( $\text{m/d}$ ),  $\rho$  is the soil bulk density ( $\text{g/cm}^3$ ),  $n$  is the effective porosity (dimensionless), and  $\lambda$  is the lumped decay rate ( $1/\text{d}$ ). Note that mass in the vapor phase was neglected in this case because of the low volatility of lindane. The curves in Figure 5 were plotted by incorporating the conventional linear isotherm and the DED model in Equation 3 (solved with a computer code by Chen et al. [37]). The figure clearly shows that if desorption were controlled by the conventional linear model, lindane in soil would decrease readily and would be below the current regulatory values in a few years under natural conditions. If this were true, we probably would not have seen the strong persistence of lindane in soil.

However, when desorption was described with a biphasic model, lindane became highly resistant—in this simulated case, the concentration in soil changed very little after 10 years of weathering.

#### Implications for soil quality standards

A sorption/desorption term is included in the models and equations used to derive soil/sediment quality standards for several ecological and human health-risk pathways. For example, the following model is adopted by the U.S. EPA and state agencies to calculate the soil quality standards protective of groundwater ingestion:

$$SQC = \left( \frac{\theta_{ws}}{\rho} + K_{oc} \cdot f_{oc} + \frac{H \cdot \theta_{as}}{\rho} \right) \cdot C_L \quad (4)$$

where  $SQC$  ( $\text{mg/kg}$ ) is the soil quality standard,  $C_L$  ( $\text{mg/L}$ ) is the maximum allowable concentration of contaminant in the soil leachate (often calculated from drinking water standard, such as the medium concentration level, by multiplying a leachate dilution factor),  $H$  ( $\text{cm}^3\text{-H}_2\text{O}/\text{cm}^3\text{-air}$ ) is the Henry's Law constant for the contaminant, and  $\theta_{as}$  ( $\text{cm}^3\text{-air}/\text{cm}^3\text{-soil}$ ) and  $\theta_{ws}$  ( $\text{cm}^3\text{-H}_2\text{O}/\text{cm}^3\text{-soil}$ ) are the volumetric air content and water content, respectively, in the vadose zone soil. The linear sorption model used in the equation (i.e., the  $K_{oc} \cdot f_{oc}$  term) is based on the assumption that the entire mass of a contaminant in soil is equally available to desorption and therefore poses the same risk to groundwater from leaching while neglecting the effect of resistant desorption. For many nonpolar hydrophobic organic contaminants, Equation 4 would be more accurate when a biphasic desorption model (e.g., Eqn. 1) is used to replace the linear model.

The  $SQC$ s of naphthalene, phenanthrene, atrazine, and lindane currently adopted in Texas and the proposed more realistic  $SQC$ s, by taking into account the effect of resistant desorption, are compared in Table 2. For more detailed discussion on how biphasic desorption models can be incorporated in Equation 4 and how to obtain the necessary parameters, the reader is referred to Chen et al. [36]. The revised  $SQC$ s for atrazine and lindane are considerably less stringent than the currently adopted  $SQC$ s, whereas for naphthalene and phenanthrene the revised standards are essentially the same as the current standards. This seems to be paradoxical (because all four chemicals exhibited significant resistant desorption) but is in fact consistent with the unique characteristic that the resistant-desorption effect is significant only in the lower concentration range. Because naphthalene and phenanthrene are much less strictly regulated than atrazine and lindane (which can be seen from the much higher medium concentration level values and thus much higher  $C_L$  values in Eqn. 4), at their respective  $C_L$  values the resistant-desorption behavior has not become significant. Therefore, it is important to note that the currently adopted  $SQC$ s for many organic contaminants might

Table 2. Current soil quality standards<sup>a</sup> versus revised standards accounting for resistant desorption

	Naphthalene	Phenanthrene	Atrazine	Lindane
Medium concentration level (mg/L)	0.49	0.73	0.003	0.0002
Current standards (mg/kg)	31.3	414	0.0248	0.00916
Revised standards (mg/kg)	31.9	414	0.417	0.847
Revised standard/current standard	1.02	1.00	16.9	92.5

<sup>a</sup> Texas, USA, Tier 1 protective concentration levels protective of groundwater ingestion, for residential areas less than 0.5 acre; Tier 1 default values were used for parameters in Equation 4.



be overly stringent (i.e., the risks of soils contaminated with these contaminants are overestimated), especially for those contaminants that are more strictly regulated, and more accurate biphasic desorption models should be used when deriving soil quality standards. It is also noteworthy that for a given contaminant the significance of resistant desorption depends on the difference between the  $K_{OC}$  value of the readily desorbable fraction ( $K_{OC}^{1st}$ ) and the  $K_{OC}$  value of the desorption-resistant fraction ( $K_{OC}^{2nd}$ ). Since the  $K_{OC}^{2nd}$  values are similar for different contaminants ( $\sim 10^{5.92}$  as mentioned above), the effect of resistant desorption is more prominent for low- $K_{OW}$  compounds (which have low  $K_{OC}^{1st}$  values) than high- $K_{OW}$  compounds (which have high  $K_{OC}^{1st}$  values). For a high- $K_{OW}$  contaminant (such as DDT) whose  $K_{OC}^{1st}$  and  $K_{OC}^{2nd}$  values are similar, the  $SQC$  calculated on the basis of the approach mentioned above would be similar to the currently adopted  $SQCs$ .

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